# Inorganic chemistry

## *Lecturer . 8*

## Bond Polarity and Electronegativity

**The electron pairs shared between two atoms *are not necessarily shared equally***

**Extreme examples:**

**1. In $Cl_2$ the shared electron pairs is shared equally**

**2. In NaCl the 3*s* electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting *of individual $Na^+$ and $Cl^-$ ions***

***For most covalent substances, their bond character falls between these two extremes***

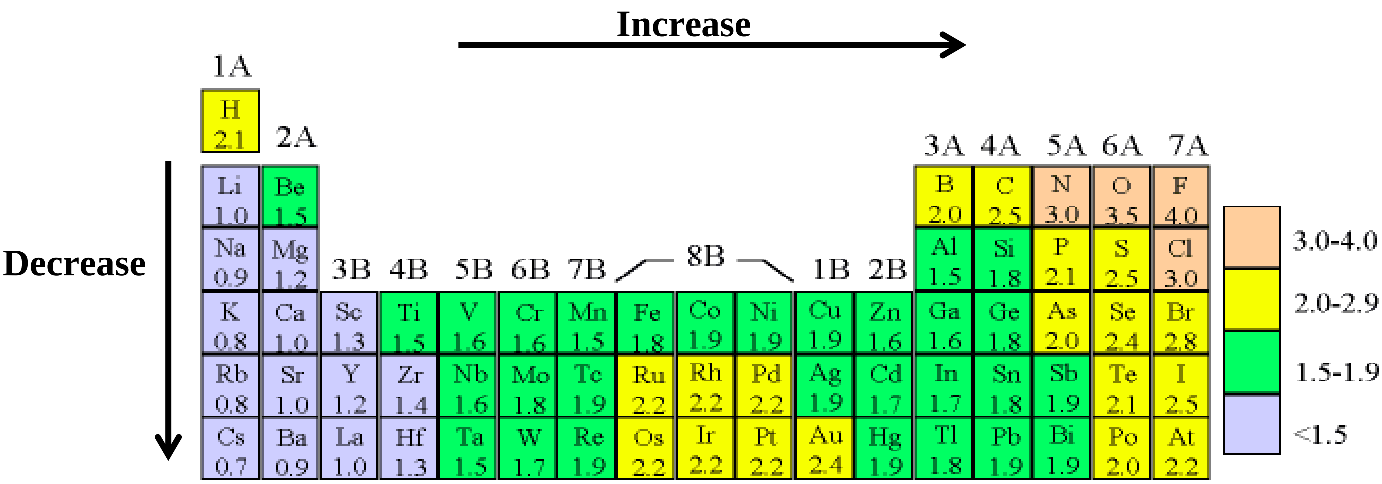
## Bond polarity

- **is a useful concept for describing the sharing of electrons between atoms**
- **A *nonpolar covalent bond* is one in which the electrons are shared equally between two atoms**
- **A *polar covalent bond* is one in which *one atom has a greater attraction for the electrons than the other atom*. If this relative attraction is great enough, then the bond is an *ionic bond***

## Electronegativity

**Electronegativity refers to the ability of an atom in a molecule to attract shared electrons**

**The Pauling scale of electronegativity:**




## Electronegativity

- **A quantity termed '*electronegativity*' is used to determine whether a given bond will be *nonpolar covalent*, *polar covalent*, or *ionic*.**

- ***Electronegativity is defined as the ability of an atom <u>in a particular molecule</u> to attract electrons to itself***

***(the greater the value, the greater the attractiveness for electrons)***

**<u>Electronegativity is a function of:</u>**

- **the atom's *ionization energy* (how strongly the atom holds on to its own electrons)**
- **the atom's *electron affinity* (how strongly the atom attracts other electrons)**

***(Note that both of these are properties of the isolated atom)***

**For example, an element which has:**

- **A large (negative) electron affinity**
- **A high ionization energy (always endothermic, or positive for neutral atoms)**

**Will:**

- **Attract electrons from other atoms**
- **Resist having its own electrons attracted away**
- **Such an atom will be highly electronegative**
- **Fluorine is the *most* electronegative element (electronegativity = 4.0), the *least* electronegative is Cesium (notice that are at diagonal corners of the periodic chart)**
- **The effective nuclear charge ($Z_{eff}$) equals the number of protons in the nucleus ($Z$), minus the average number of electrons ($S$) that are between the electron in question and the nucleus**

$$Z_{eff} = Z - S$$

**<u>General trends:</u>**

- **Electronegativity *increases from left to right* along a period**
- **For the representative elements (*s* and *p* block) the electronegativity *decreases as you go down* a group**
- **The transition metal group is not as predictable as far as electronegativity**

**<u>Electronegativity and bond polarity</u>**

***We can use the difference in electronegativity between two atoms to gauge the polarity of the bonding between them***

| **Compound** | **$F_2$** | **HF** | **LiF** |
|---|---|---|---|
| **Electronegativity Difference** | **4.0 - 4.0 = 0** | **4.0 - 2.1 = 1.9** | **4.0 - 1.0 = 3.0** |
| **Type of Bond** | **Nonpolar covalent** | **Polar covalent** | **Ionic (non-covalent)** |

- **In $F_2$ the electrons are shared equally between the atoms, the bond is nonpolar covalent**
- **In HF the fluorine atom has greater electronegativity than the hydrogen atom.**

***The sharing of electrons in HF is unequal: the fluorine atom attracts electron density away from the hydrogen (the bond is thus a polar covalent bond)***

**<u>The H-F bond can thus be represented as:</u>**

$$\overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{F}} \qquad \text{or} \qquad \overset{+\!\!\longrightarrow}{\mathrm{H - F}}$$

- **The 'δ+' and 'δ-' symbols indicate *partial* positive and negative charges.**
- **The arrow indicates the "pull" of electrons off the hydrogen and towards the more *electronegative* atom**
- **In lithium fluoride the much greater *relative* electronegativity of the fluorine atom completely strips the electron from the lithium and the result is an ionic bond (no sharing of the electron)**

***A general rule of thumb for predicting the type of bond based upon electronegativity differences:***

- **If the electronegativities are equal (i.e. if the electronegativity difference is 0), the bond is <u>non-polar covalent</u>**
- **If the difference in electronegativities between the two atoms is greater than 0, but less than 2.0, the bond is <u>polar covalent</u>**
- **If the difference in electronegativities between the two atoms is 2.0, or greater, the bond is <u>ionic</u>**

**Bond Polarity**

**A polar bond can be pictured using partial charges:**

$$\underset{2.1}{\overset{\delta^{+}}{\mathrm{H}}} — \underset{3.0}{\overset{\delta^{-}}{\mathrm{Cl}}} \qquad \Delta\delta = 0.9$$

| Electronegativity Difference | Bond Type |
|---|---|
| 0 – 0.5 | Nonpolar |
| 0.5 – 2.0 | Polar |
| 2.0 ↑ | Ionic |

## Lewis Dot Structures ( VSEPR )

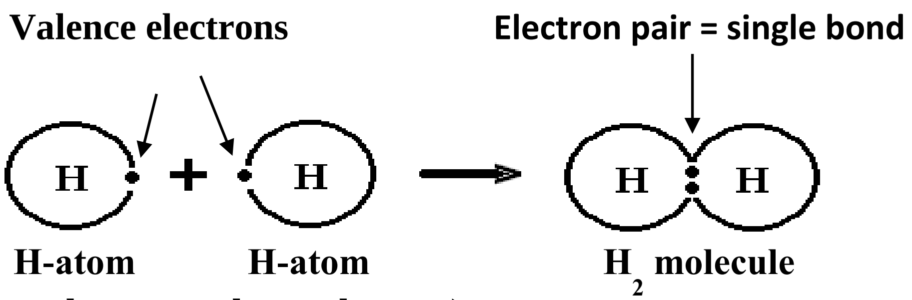
**G. N. Lewis was probably the best chemist who never won the Nobel Prize .**

**G.N. Lewis**

- **reasoned that an atom might attain a noble gas electron configuration by *sharing* electrons**
- ***A chemical bond formed by sharing a pair of electrons is called a covalent bond***

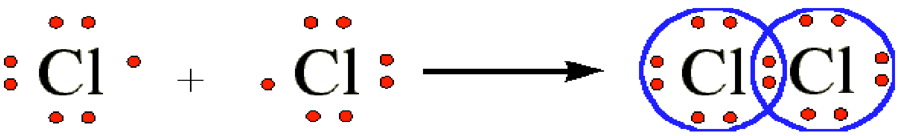
## Lewis Dot Structures (revision)

**Lewis dot structures present a simple approach to bonding that allows us to rationalize much molecular structure. The idea is that atoms share electrons in the valence shell to form the chemical bond, with one pair of electrons per bond. Note that each H-atom has two electrons, which is the structure of He, the next inert gas.**




**(Each H-atom has one valence electron)**

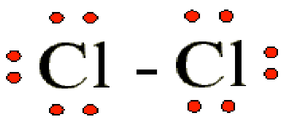
**When two chlorine atoms covalently bond to form $Cl_2$, the following sharing of electrons occurs:**

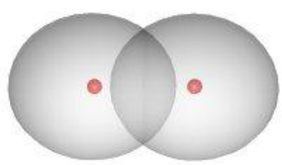



**Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon.**

**In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:**

H - H



**The shared electrons are not located in a fixed position between the nuclei. In the case of the $H_2$ compound, the electron density is concentrated between the two nuclei:**

***The two atoms are bound into the $H_2$ molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them***

**For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:**

| Element | Group | Valence electrons | Bonds needed to form valence octet |
|---|---|---|---|
| F | 7A | 7 | 1 |
| O | 6A | 6 | 2 |
| N | 5A | 5 | 3 |
| C | 4A | 4 | 4 |

## Drawing Lewis Structures

**The general procedure...**

**1.** ***Sum the valence electrons from all atoms***

- **Use the periodic table for reference**
- **Add an electron for each indicated negative charge, subtract an electron for each indicated positive charge**

**2.** ***Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond***

- **You may need some additional evidence to decide bonding interactions**
- **If a central atom has various groups bonded to it, it is usually listed first: $CO_3^{2-}$, $SF_4$**
- **Often atoms are written in the order of their connections: HCN**

**3.** ***Complete the octets of the atoms bonded to the central atom (H only has two)***

**4.** ***Place any leftover electrons on the central atom (even if it results in more than an octet)***

**5.** ***If there are not enough electrons to give the central atom an octet, try multiple bonds (use one or more of the unshared pairs of electrons on the atoms bonded to the central atom to form double or triple bonds)***

## Drawing Lewis Structures

- **Sum the valence electrons from all atoms .**
  **Add one for each negative charge and subtract one for each positive charge.**

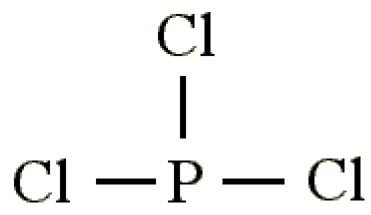
- **Draw a skeleton structure with atoms attached by single bonds.**
- **Complete the octets of atoms bound to the central atom.**
- **Place extra electrons on the central atom.**
- **If the central atom doesn't have an octet, try forming multiple bonds .**

**Draw the Lewis structure of phosphorous trichloride ($PCl_3$)**

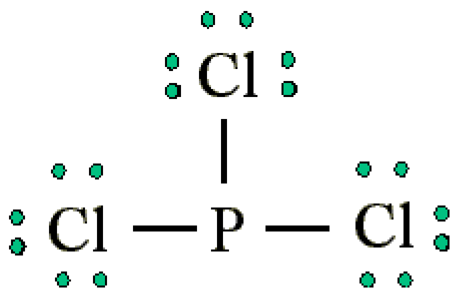
**This is an example of a central atom, P, surrounded by chlorine atoms**

**1. We will have 5(P) plus 21 (3*7, for Cl), or 26 total valence electrons**

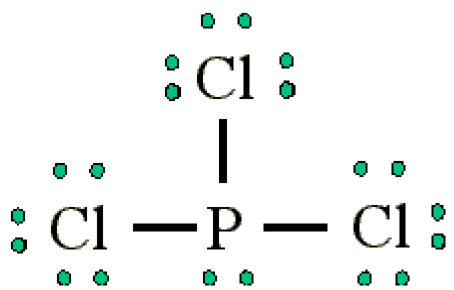
**2. The general symbol, starting with only single bonds, would be:**



**3. Completing the octets of the Cl atoms bonded to the central P atom:**



**4. This gives us a total of (18 electrons) plus the 6 in the three single bonds, or 24 electrons total. Thus we have 2 extra valence electrons which are not accounted for. We will place them on the central element:**

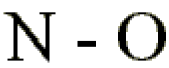


**5. The central atom now has an octect, and there is no need to invoke any double or triple bonds to achieve an octet for the central atom. We are finished.**

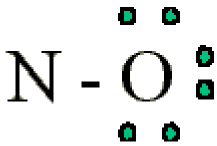
**<u>Draw the Lewis structure for the $NO^+$ ion</u>**

**1. We will have 5 (N) plus 6 (O) minus 1 (1+ ion), or 10 valence electrons**

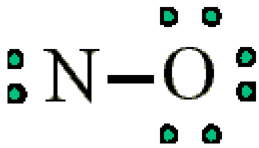
**2. The general structure starting only with single bonds would be:**



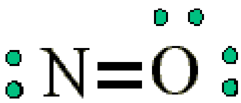
**3. Completing the octet of the O bonded to N:**



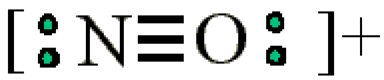
**4. This gives us a total of 6 plus 2 for the single bond, or 8 electrons. There are 2 unaccounted for electrons and we will place them on the N:**



**5. There are only 4 atoms on the N atom, not enough for an octet, so lets try a double bond between the N and O:**



**The oxygen still has an octet, but the N only has 6 valence electrons, so lets try a triple bond:**

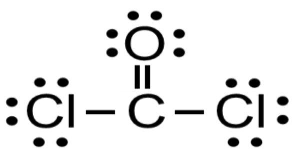


**Each atom now has a valence octet. We are finished.**

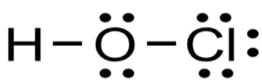
***The brackets with the + symbol are used to indicate that this is an ion with a net charge of 1+***

**<u>Drawing Lewis Structures</u>**

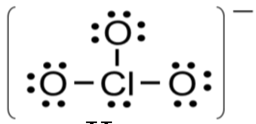
**$COCl_2$** **24 e-**



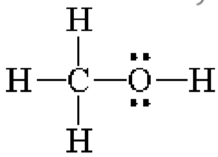
**HOCl** **14 e-**



**$ClO_3^-$** **26 e-**



**$CH_3OH$** **14 e-**

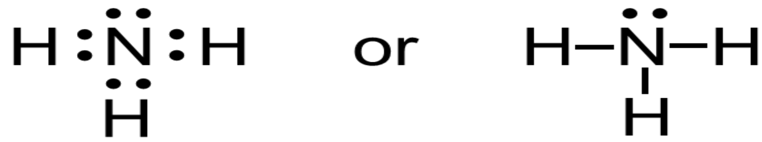


**<u>Draw Lewis structures for:</u>**

HF

$H_2O$

$NH_3$



$CH_4$

**<u>Formal Charge</u>**

**In some cases we can draw *several* different Lewis structures which fulfill the octet rule for a compound. Which one is the most reasonable?**

**One method is to tabulate the valence electrons around each atom in a Lewis structure to determine the *formal charge*. The formal charge is the charge that an atom in a molecule would have if we considered each atom to have the same electronegativity in a compound.**

**To calculate formal charge, assign electrons to their respective atoms as follows:**

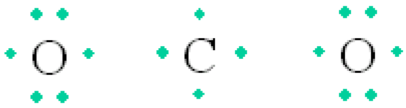
1. **All of the unshared electrons are assigned to the atom on which they are found**
2. **The bonding electrons are divided up equally between each atom involved in the bond**
3. **The number of valence electrons expected in the isolated atom is compared to the actual number of electrons assigned from the Lewis structure:**

***The formal charge equals the number of valence electrons in the isolated atom, minus the number of electrons assigned in the Lewis structure***

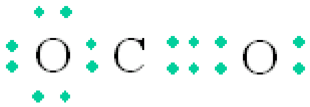
**Example: Carbon Dioxide ($CO_2$)**

**Carbon has 4 valence electrons**

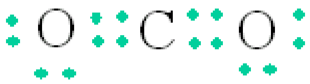
**Each oxygen has 6 valence electrons, therefore our Lewis structure of $CO_2$ will have 16 electrons:**



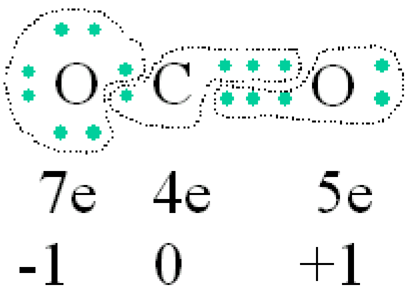
**One way we could draw the Lewis structure is:**

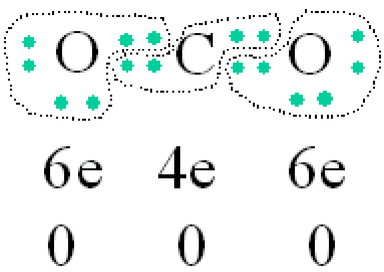


**Another way we could draw the Lewis structure is:**



**Both structures fulfill the octet rule. But what are the formal charges?**




**Which structure is correct? In general, when several Lewis structures can be drawn the most stable structure is the one in which:**

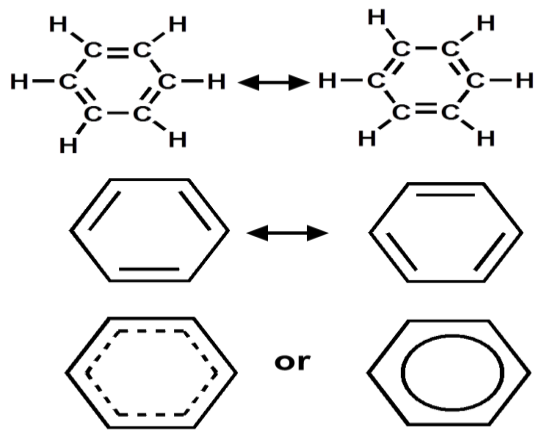
- **The formal charges are the smallest**
- **Any negative charge is found on the most electronegative atom**

**In the above case, the second structure is the one with the smallest formal charges (i.e. 0 on all the atoms).**

- **Furthermore, in the first possible Lewis structure the carbon has a formal charge of 0 and one of the oxygens it is bonded to has a formal charge of +1.**
- **Oxygen is more electronegative than Carbon, so this situation would seem unlikely.**

**It is important to remember that formal charges do not represent the actual charges on the atoms. Actual charges are determined by the electronegativity of the atoms involved.**

**<u>Resonance in benzene.</u>**



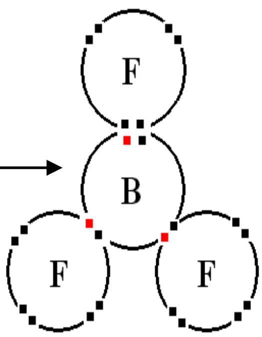

**Short-hand versions for the benzene ring**

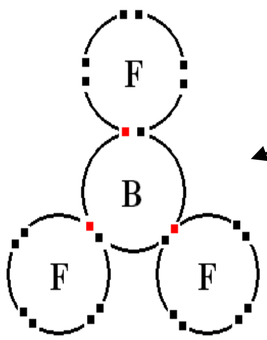
- **There are two canonical structures for benzene, which means that the C to C bonds have a bond order of (2+1)/2 = 1.5.**
- **The benzene ring has a very high stability due to this resonance, which is called aromaticity.**

**<u>Exceptions to the octet rule</u>**

**$BF_3$. This can be written as $F_2B{=}F$ with three resonance structures. To complete its octet, $BF_3$ readily reacts with e.g. $H_2O$ to form $BF_3.H_2O$.**
**The actual structure of $BF_3$ appears not to involve a double bond and does not obey the octet rule:**

**Possible resonance structure for $BF_3$, but is not important as this would involve the very electronegative F donating e's to B**

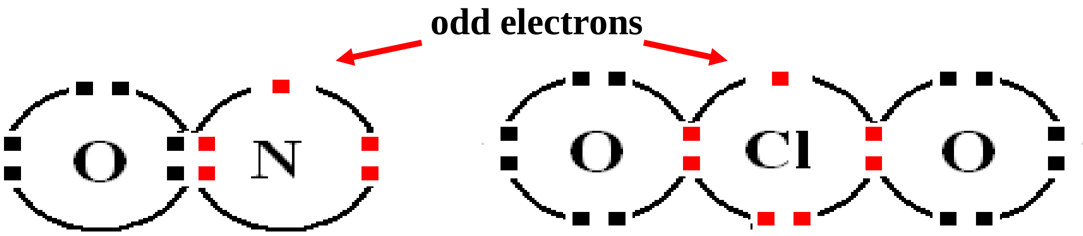



**Best representation of $BF_3$ with B having only 6 electrons in its valence shell**

<u>Exceptions to the octet rule: free radicals</u>

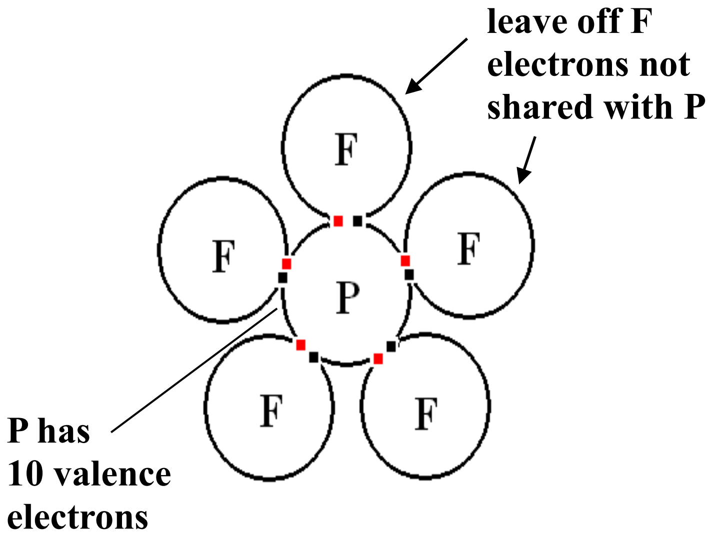
**There are some molecules that do not obey the octet rule because they have an odd number of electrons. Such molecules are very reactive, because they do not achieve an inert gas structure, and are known as free radicals. Examples of free radicals are chlorine dioxide, nitric oxide, nitrogen dioxide, and the superoxide radical:**

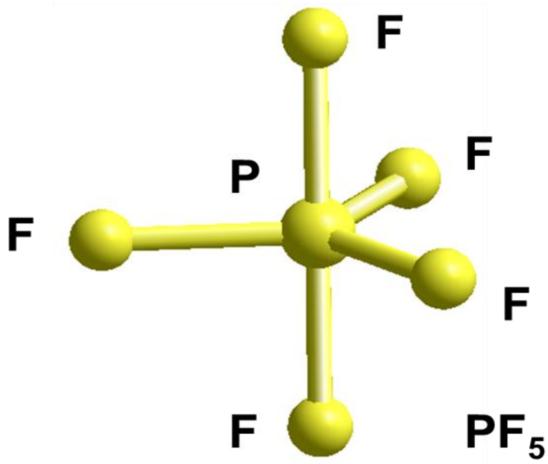



**<u>Exceptions to the Octet rule:</u> Heavier atoms (P, As, S, Se, Cl, Br, I) may attain more than an octet of electrons:**

**<u>Example:</u> $PF_5$.**

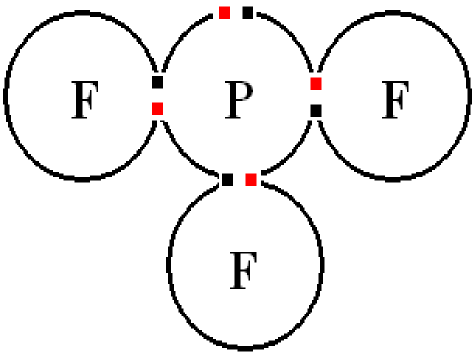
**In $PF_5$, the P atom has ten electrons in its valence shell, which occurs commonly for heavier non-metal atoms:**

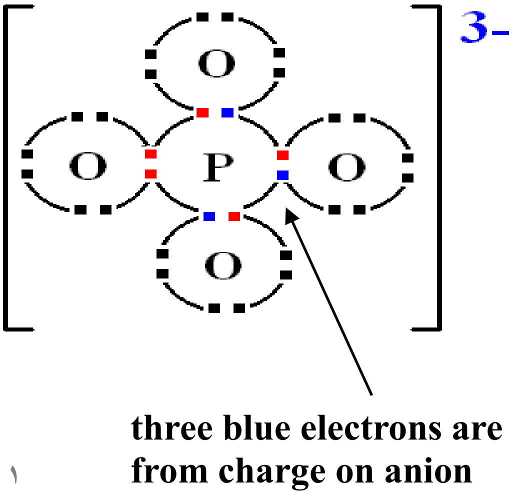


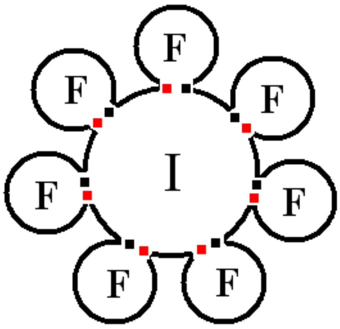

**<u>Many phosphorus compounds do obey the octet rule:</u>**

**$PF_3$ and $[PO_4]^{3-}$ :**

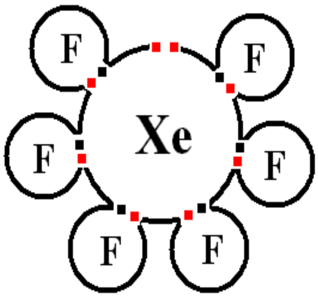


**<u>Some compounds greatly exceed an octet of electrons:</u>**



**$IF_7$**



**$XeF_6$**

**(both I and Xe have 14 valence e's)**

**(Think about $[XeF_8]^{2-}$ )**

**<u>Q : Draw an electron dot structure for</u>**

**(a) Methylene chloride , $CH_2Cl_2$ .**
**(b) Chloroform , $CHCl_3$ .**
**(c) Carbon tetrachloride, $CCl_4$ .**

## <u>Exceptions to the Octet Rule</u>

***There are three general ways in which the octet rule breaks down:***

**1. Molecules with an odd number of electrons**

**2. Molecules in which an atom has less than an octet**

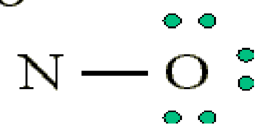
**3. Molecules in which an atom has more than an octet**

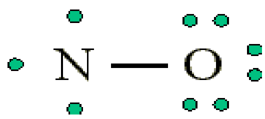
### <u>1. Odd number of electrons</u>

**Draw the Lewis structure for the molecule nitrous oxide (NO):**

**1. Total electrons: 6+5=11**

**2. Bonding structure:** 

**3. Octet on "outer" element:** 

**4. Remainder of electrons (11-8 = 3) on "central" atom:** 

**5. There are currently 5 valence electrons around the nitrogen. A double bond would place 7 around the nitrogen, and a triple bond would place 9 around the nitrogen.**

***We appear unable to get an octet around each atom***

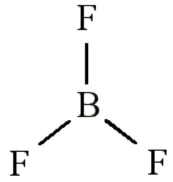
## 2. Molecules in which an atom has less than an octet

**Less than an octet *(most often encountered with elements of Boron and Beryllium*)**

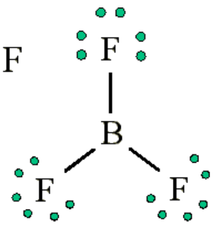
**Draw the Lewis structure for boron trifluoride ($BF_3$):**

**1. Add electrons (3*7) + 3 = 24**

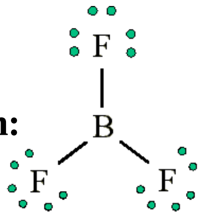
**2. Draw connectivities:**



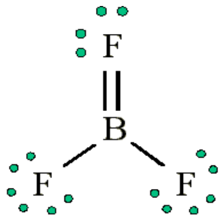
**3. Add octets to outer atoms:**



4. **Add extra electrons (24-24=0) to central atom:**



**5. Does central electron have octet?**



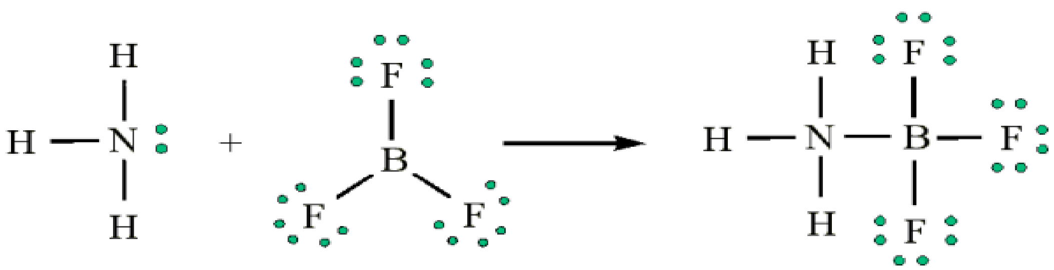
- **NO. It has 6 electrons**
- **Add a multiple bond (double bond) to see if central atom can achieve an octet:**

**6. The central Boron now has an octet (there would be three resonance Lewis structures)**

***However...***

- **In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.**
- **The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.**
- **Thus, *the structure of $BF_3$, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

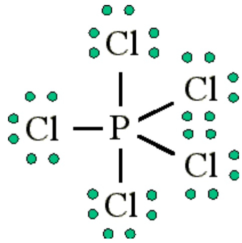
**$BF_3$ reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:**



**3. Molecules in which an atom has more than an octet**

**More than an octet *(most common example of exceptions to the octet rule*)**

**$PCl_5$ is a legitimate compound, whereas $NCl_5$ is not.**



***Expanded valence shells are observed only for elements in period 3***

***(i.e. n=3) and beyond***

- **The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals)**
- **Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2)**

**The orbital diagram for the valence shell of phosphorous is:**


***Third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons***

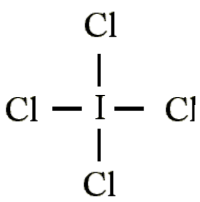
**<u>Size is also an important consideration:</u>**

- **The larger the central atom, the larger the number of electrons which can surround it**
- **Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.**

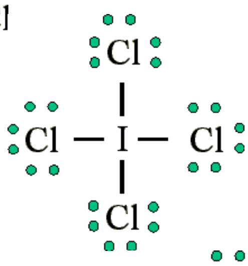
**Draw the Lewis structure for $ICl_4^-$**

**1. Count up the valence electrons: 7+(4*7)+1 = 36 electrons**

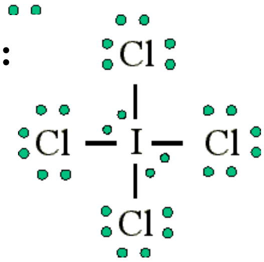
**2. Draw the connectivities:**



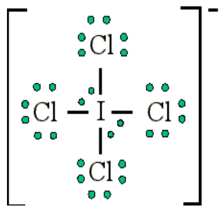
**3. Add octet of electrons to outer atoms:**



**4. Add extra electrons (36-32=4) to central atom:**

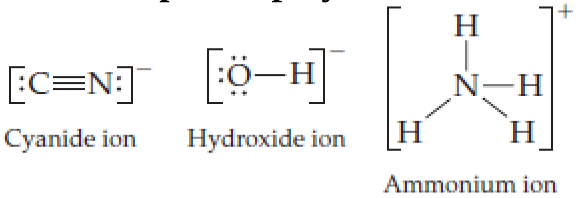


5. **The $ICl_4^-$ ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)**



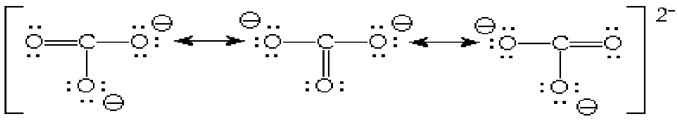
## RESONANCE STRUCTURES

■ **In Figure (a) represents the electron dot structures for cyanide ion, ammonium ion, and hydroxide ion are three examples of polyatomic ions.**




**(a)**

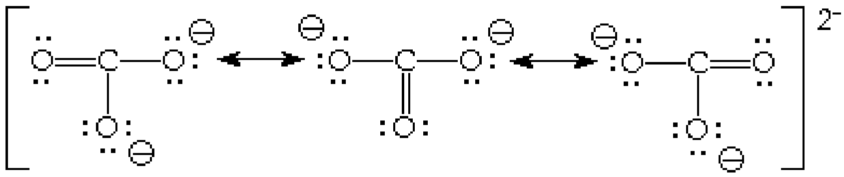
**Three equivalent Lewis structures (formal charges are included) can be drawn for the carbonate ion.**



■ **In Figure (b) Three resonance stabilized forms of carbonate polyatomic ion, $CO_3^{2-}$**

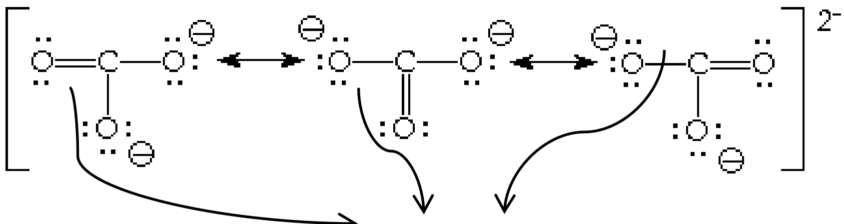
**HOW ?! Follow Lewis Structure rules**

**carbon (C) has four valence electrons x 1 carbon = 4 *e*$^-$**
**oxygen (O) has six valence electrons x 3 oxygens = 18 *e*$^-$**
**The ion has an overall negative two charge so we add 2 *e*$^-$ to give a total of 24 *e*$^-$ to be placed in the Lewis structure.**



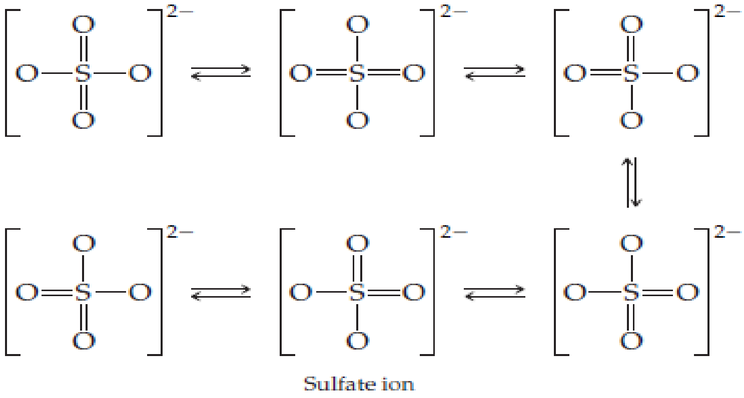
**(b)**

- **This affords a bond order for the carbon - oxygen bond of 1 1/3. (4 bonds averaged over three structures.)**



$$\textbf{Bond Order} = \frac{2 + 1 + 1}{3\ \text{structures}} = 1\ 1/3$$

■ **In Figure (c) Six resonance stabilized forms of the sulfate polyatomic ion.**



(c)

**TABLE 4.1 Procedure for Drawing a Molecule's Electron Dot Structure**

1. **Count the total number of valence electrons in the molecule.**
2. **Draw the molecule's skeletal structure from its molecular formula.**
3. **Calculate the number of electrons used to show the skeletal structure, and subtract this number from the total calculated in step 1.**
4. **Assign the remaining electrons to atoms connected to the central atom, following the octet rule for all atoms except H (which should have a duet of electrons).**
5. **If you have any electrons left after completing step 4, place them on the central atom. If you have run out of electrons before the central atom has an octet, move one or more nonbonding electron pairs from an adjoining atom to the central atom to form a multiple bond.**
6. **Check that every atom has an octet of electrons (duet for H) and that all the valence electrons calculated in step 1 have been placed.[a]**

**Q. Why we are dealing with do structures again**

**There are two reasons for this.**

■ **First, we are dealing with ions, not neutral molecules and the rules governing electron dot structures apply only to uncharged molecules. (Now you know why.) For example, nitrogen makes four bonds (not three) when it has a charge of + 1, as it does in the ammonium ion of Figure (a) .**

■ **Second, most simple polyatomic ions are not organ-ic molecules because they are not based on a carbon-chain framework. Rather, they are *inorganic* compounds that happen sometimes to contain carbon. Thus, when you leave the realm of organic chemistry, rule 2 no longer applies.**

- **Inorganic compounds have a wider range of structures available to them because they are made up of a wider variety of elements than organic compounds are.**
- **For example, the permanganate ion, $MnO_4^-$, contains manganese, an element not found in most organic molecules.**